

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : E21D 9/06, C09K 7/08	A1	(11) International Publication Number: WO 99/18330 (43) International Publication Date: 15 April 1999 (15.04.99)
(21) International Application Number: PCT/EP98/05905 (22) International Filing Date: 15 September 1998 (15.09.98) (30) Priority Data: 9720846.6 2 October 1997 (02.10.97) GB (71) Applicant (for all designated States except US): MBT HOLD- ING AG [CH/CH]; Vulkanstrasse 110, CH-8048 Zürich (CH). (72) Inventor; and (75) Inventor/Applicant (for US only): ELLENBERGER, Peter [CH/CH]; Rebbergstrasse 97, CH-8706 Feldmeilen (CH).		(81) Designated States: AU, BR, CN, JP, SG, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FOAMING COMPOSITION (57) Abstract <p>A method of boring a tunnel through a stratum by means of a shield tunnelling apparatus, the process comprising the injection into the stratum at the cutting face of an aqueous material comprising: (a) from 0.005–0.05 % by weight of a polyethylene oxide of weight-average molecular weight from 2,000,000 to 8,000,000; (b) from 0.05–0.5 % by weight of a sulphate-containing anionic surfactant. The method is effective even in difficult soils.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

FOAMING COMPOSITION

5 This invention relates to tunnel boring and to compositions for use therein.

Shield tunnel boring machines are increasingly used in the boring of tunnels, because they offer many advantages such as the ability to bore in a wide variety of strata. A shield boring machine comprises a circular rotatable cutting head mounted on a cylindrical
10 shield of similar diameter such that its axis of rotation coincides with the longitudinal axis of the shield. Within the shield there are contained means for feeding materials to the cutting head and means for conveying away the soil. Such machines perform well when the strata through which a tunnel is being bored is relatively hard and firm, but they do not perform so well in soft and crumbly strata which can make soil removal very difficult.
15 One way of seeking to overcome this problem is to apply a consolidation agent to the soil via the cutting head. This stabilises the soil, allowing boring to be more easily effected and the soil to be more easily removed.

Known stabilising agents have included bentonite slurries and polymer suspensions. These
20 can lead to problems in certain soils, largely because they increase the soil water content appreciably. Some soils (such as clays) can become sticky and difficult to remove and clog up the cutting head, resulting in a substantial loss in efficiency. In a more recent development, polymer foams have been suggested. These have the advantage that considerably less fluid is placed in the soil per given volume. A typical foam formulation
25 will comprise a foaming agent and a foam stabilising agent, the latter generally a surfactant. Thus, in operation, the foam is injected from ports in the cutting head into the face being bored.

It has now been found that a particular foaming material gives especially efficacious
30 results. The invention therefore provides a method of boring a tunnel through a stratum by means of a shield tunnelling apparatus, the process comprising the injection into the stratum at the cutting face of an aqueous material comprising

(a) from 0.005-0.05% by weight of a polyethylene oxide of weight-average molecular weight from 2,000,000 to 8,000,000; and

(b) from 0.05-0.5% by weight of a sulphate-containing anionic surfactant.

5

The invention additionally provides a foaming material adapted to assist the conveyance of soil from the cutting face of a shield tunneling apparatus, comprising

(a) from 0.005-0.05% by weight of a polyethylene oxide of weight-average molecular
10 weight from 2,000,000 to 8,000,000; and

(b) from 0.05-0.5% by weight of a sulphate-containing anionic surfactant.

Polyethylene oxides (PEO) are well-known items of commerce and a suitable material
15 may be selected from the wide range available. Typical examples are the "Polyox" (trade mark) materials of Union Carbide. The anionic surfactant may be selected from any such sulphate-containing surfactant known to the art. A particularly preferred type is polyoxyalkylene alkyl ether sulphate, where the polyalkyleneoxide chain has an average chain length of 2-3 alkylene oxide units. Typical commercial materials include the
20 "Alscope" (trade mark) series of Toho Chemical Industry Co.

Preferably the quantities of PEO and surfactant present are from 0.02 to 0.04% and from 0.15 to 0.4% by weight, respectively. Most preferably, the PEO quantity is from 0.03-0.04%.

25

The rest of the aqueous material is generally water, but other art-recognised ingredients (such as biocides and complexing agents) can be added in art-recognised quantities. In a preferred embodiment of the invention, the aqueous material additionally comprises urea, to the extent of from 0.03-0.8%, preferably 0.06-0.25% by weight. The invention
30 therefore also provides a tunnelling foaming additive consisting essentially of polyethylene oxide, sulphate-containing anionic surfactant and urea and water.

Another especially useful ingredient is a foam improver. Foam improvers are materials which are well known in the art for their ability to stabilise foams. They are typically amines with long fatty acid chains derived from natural fats and oils, for example coconut
5 oil.

The aqueous material may be prepared and stored in advance as a single material, but it is preferred to provide it as two components which are mixed prior to use. In this case, one component comprises PEO and surfactant, and the other is a dilute aqueous solution of
10 PEO, typically at a weight concentration of from 0.007-0.015%, preferably from 0.015-0.06%. Both of course contain sufficient water to ensure that they are sufficiently fluid, and sufficient of the essential ingredients to give on mixing proportions of the size listed hereinabove - appropriate mixtures with respect to molecular weights and proportions are readily determined. The water content of the aqueous material should be such that it has a
15 viscosity as measured by the Bohlin System 3 apparatus, using spindle 1 of from 600-1200 mPa.s., and in the case of the two component embodiment, the water contents of the individual components should be such as to achieve this. The two-component embodiment is exceptionally storage-stable.

20 In operation, the aqueous material is supplied to the machine, where it is diluted to typically a 3% solution of total aqueous material in water and foamed by conventional means and injected into the tunnel face via ports in the cutting head. In addition, foam can also be injected from ports in the shield to strengthen the tunnel walls.

25 The invention is further described with reference to the following non-limiting worked examples.

Example 1

The following materials are blended

5		<u>parts by weight</u>
	polyoxyalkylene alkyl ether sulphate ¹	8.58
	urea	5.00
	polyethylene oxide ²	1.20
	biocide ³	0.02
10	complexing agent ⁴	0.02
	water	85.18

¹ "Alscope" W 140

² "Polyox" (trade mark) WSR-301

15 ³ "Biotack" (trade mark)

⁴ "Clewat" (trade mark)

This composition provides a concentrate for use, which use is demonstrated in Example 2.

20 Example 2

Testing of the composition of Example 1 on a soil.

The soil which is used is taken from Madrid where the tunnelling for the new metro has
25 been especially difficult. The experiment consists of taking four 1000g-sized samples of
this soil (a heavy clay), adding a material to three of these in an attempt to make it
removable, agitating the mixture in a Hobart mixer for 3 minutes and then checking the
viscosity by means of a Haake VT02 Viscometer. The stickiness of the material in the
Hobart mixing bowl is also assessed.

To each of three 1000g samples are added one of the following:

- (a) 65g water
- (b) 65g of a 3% solution of a foaming agent "Rheocell" (trade mark), foamed 1:10 with air (1 volume solution to 9 volumes air)
- 5 (c) 65g of a 3% solution of the composition of Example 1 foamed 1:10 with air

In addition to the viscosity (which is an indication of the ease of soil removal from a cutting head), the stickiness of the material is assessed comparatively when cleaning out the mixing bowls. The ratings for stickiness are

10

- 1 - very sticky, soil will not pour from bowl and is removable only with difficulty
- 2 - sticky, soil will not pour from bowl, but can be removed relatively easily
- 3 - not sticky, most soil pours out of bowl and the little residue remaining is easily removed.

15

The results are as follows:

	<u>Viscosity (poise)</u>	<u>Stickiness</u>
mud alone	1000 ¹	1
20 (a) mud and water	300 ¹	1
(b) mud and foaming agent	50 ²	2
(c) mud and Example 1 composition	50 ²	3

25 ¹ The measurements are made using a No. 2 spindle, used for thick liquids and paste.

² A larger spindle (No.1) is used for thinner liquids and pastes.

It can be seen that the composition according to the invention gives substantial
 30 improvements in both viscosity and stickiness, even though a bigger spindle (which normally gives a higher viscosity reading than a smaller one) was used.

Example 3

Example of a two-component system

5

A two-part system is formed by using 1 part of the composition of Example 1 with up to 10 parts of water which contain 1% by weight of "Polyox" WSR-301. The proportion of this polyethylene oxide solution is adjusted, depending on the water content of the mud involved.

10

When tested according to the procedure of Example 2, the composition gives the same excellent results as that of the composition of Example 1.

Examples 4-7

15

A number of compositions according to the invention are prepared and tested according to the procedure set out in Example 2.

The compositions are shown in the following table:

20

<u>Example No.</u>	<u>sulphate- containing surfactant</u>	<u>polyethylene oxide</u>	<u>complexing agent</u>	<u>foam improver</u>
4	Zetesol NL2	Polyox WSR-301	Cublen K2523	Urea

5	Sulfetal Cjot 60	Polyox WSRN-60K	Masquol P430 NA	Aromox MCD-W
6	Hostaspur OS-1	"	Sequion 50K33	Quiminox QL
7	Empicol LX 42	Polyox WSR-301	Cublen AP1	Aromox C/12-W

The materials used are as follows:

5 "Zetesol" (trade mark) NL2 (ex Zschimmer & Schwarz) - sodium lauryl ether sulphate.

"Sulfetal" (trade mark) Cjot 60 (ex Zschimmer & Schwarz) -
monoisopropanolammonium lauryl sulphate.

10 "Hostaspur" (trade mark) OS-1 (ex Clariant) - sodium oleyl sulphonate.

"Empicol" (trade mark) LX 42 (ex Albright & Wilson) - sodium lauryl sulphate.

"Polyox" (trade mark) WSRN-60K (ex Union Carbide) - polyethylenoxide, molecular
15 weight (weight-average) about 2 million.

"Polyox" WSR-301 - polyethylene oxide, molecular weight (weight-average) about 4
million.

20 "Cublen" (trade mark) K2523 (ex Zschimmer & Schwarz) - tripotassium hydroxyethane
diphosphonic acid.

"Masquol" (trade mark) P 430 Na (ex Protex) - hexasodium ethylenediamine tetra(methylenephosphonic) acid.

5 "Sequion" (trade mark) 50 K 33 (ex Bozzetto) - hexapotassium ethylenediamine tetra(methylenephosphonic) acid.

"Aromox" (trade mark) C/12-W (ex Akzo-Nobel) - coco-bis-(2-hydroxyethyl) amine oxide.

10 "Aromox" MCD-W - cocodimethylamine oxide.

"Quiminox" (trade mark) QL (ex Qimidroga) cocodimethylamine oxide.

The test results obtained are rated 3, as are those of the compositions of Examples
15 1 and 3.

Claims:

1. A method of boring a tunnel through a stratum by means of a shield tunnelling apparatus, the process comprising the injection into the stratum at the cutting face
5 of an aqueous material comprising
- (a) from 0.005-0.05% by weight of a polyethylene oxide of weight-average molecular weight from 2,000,000 to 8,000,000
- 10 (b) from 0.05-0.5% by weight of a sulphate-containing anionic surfactant.
2. A method according to claim 1, wherein the sulphate-containing anionic surfactant is a polyoxyalkylene alkyl ether sulphate, where the polyalkyleneoxide chain has an average chain length of 2-3 alkylene oxide units.
- 15 3. A method according to claim 1, wherein the quantities of polyethylene oxide and surfactant present in the aqueous material are from 0.02-0.04% and from 0.15-0.4% by weight, respectively.
- 20 4. A method according to any one of claims 1-3, wherein the aqueous material additionally comprises urea.
5. A method according to any one of claims 1-3, wherein the aqueous material additionally comprises a foam booster.
- 25 6. A foaming material adapted to assist the conveyance of soil from the cutting face of a shield tunnelling apparatus, comprising
- (a) from 0.005-0.05% by weight of a polyethylene oxide of weight-average
30 molecular weight from 2,000,000 to 8,000,000
- (b) from 0.05-0.5% by weight of a sulphate-containing anionic surfactant.

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/EP 98/05905

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E21D9/06 C09K7/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 E21D C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 90 00187 A (J.PIERCE) 11 January 1990 see page 4, line 13 - line 30 see page 7, line 4 - page 9, line 14 see page 10, line 19 - page 11, line 2 see claims 1-4	1-6
Y	US 4 247 405 A (D.R. WIER) 27 January 1981 see column 2, line 42 - column 3, line 60; claims 1-7; example II	1-6
Y	US 3 215 200 A (W.H.KIRKPATRICK) 2 November 1965 see column 2, line 22 - column 3, line 23 see column 5, line 42 - line 73; claims 1,2	1-6
A	FR 2 690 709 A (SEPPIC) 5 November 1993 see claims 1-	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents :**

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

3 February 1999

Date of mailing of the international search report

10/02/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Boulon, A

INTERNATIONAL SEARCH REPORT

Int. Patent Application No.

PCT/EP 98/05905

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 008, no. 098 (C-221), 9 May 1984 & JP 59 015476 A (SUMITOMO KAGAKU KOGYO KK), 26 January 1984 see abstract</p> <p>-----</p>	1-6

INTERNATIONAL SEARCH REPORT

information on patent family members

Inte Application No

PCT/EP 98/05905

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9000187 A	11-01-1990	US 4959164 A	25-09-1990
		AU 609689 B	02-05-1991
		AU 3705789 A	04-01-1990
		US 5196401 A	23-03-1993
US 4247405 A	27-01-1981	NONE	
US 3215200 A	02-11-1965	NONE	
FR 2690709 A	05-11-1993	AT 142743 T	15-09-1996
		AU 4263393 A	29-11-1993
		DE 69304691 D	17-10-1996
		DE 69304691 T	13-02-1997
		DK 638137 T	30-09-1996
		EP 0638137 A	15-02-1995
		ES 2092307 T	16-11-1996
		WO 9322538 A	11-11-1993
		GR 3021184 T	31-12-1996
		NO 944051 A	27-12-1994